

## PATENT SPECIFICATION

(11) 1388 909

1388 909

- (21) Application N. 53442/72 (22) Filed 20 Nov. 1972  
 (31) Convention Application No. 215092 (32) Filed 3 Jan. 1972 in  
 (33) United States of America (US)  
 (44) Complete Specification published 26 March 1975  
 (51) INT CL: E21B 43/22  
 (52) Index at acceptance: E1P 44  
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## (54) FRACTURING FLUIDS

(71) We, MARATHON OIL COMPANY, of 539 South Main Street, Findlay, Ohio 45840, United States of America, a corporation organized and existing under the laws of the State of Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns fracturing fluids which have a characteristic of exhibiting a viscosity increase upon temperature increase. These fluids may be used to fracture subterranean formations, especially those formations at temperatures above ambient wherein a viscous fracturing fluid is desired.

The prior art has generally experienced that the viscosity of fracturing fluids decreases upon a temperature increase. That is, normal fracturing fluids, when injected into a formation are heated as the fluids progress down the well bore and, as a result, they lose their viscosity characteristics. Such is undesirable when fracturing subterranean reservoirs at substantially higher temperatures than ambient. Also, when such high temperatures are encountered, if the fracturing fluids are designed to have a relatively high viscosity at reservoir temperatures, the viscosities at ambient temperature are generally so high that very large energy requirements are necessary to fracture the formation. In most cases, fracturing of reservoirs at high temperatures has generally proved difficult because a fracturing fluid of sufficient viscosity at the reservoir rock face cannot be injected and efficiently pumped into the formation.

The fracturing fluid of the invention generally permits the fracturing of reservoirs at high temperatures and also generally permits minimum surface energies required to fracture the formation.

We have discovered a novel characteristic of particular non-Newtonian fluids comprised of surfactant, preferably petroleum sulfonate, aqueous medium, hydrocarbon, optionally cosurfactant and/or electrolyte which exhibit

a viscosity increase upon a temperature increase. These systems have the capability of solubilizing oil and water as well as exhibiting relatively large viscosities at high temperatures. Other additives compatible with the components of the system can be added to impart desired characteristics, e.g. propping agents, water-soluble polymers, etc. Also, the fracturing fluids by virtue of their viscoelastic properties generally exhibit drag reduction wherein a higher flow rate is obtained with a given pressure drop than would be predicted by viscous flow theory.

The present invention provides a process of hydraulically fracturing a subterranean hydrocarbon-bearing formation penetrated by at least one well, the formation being at a temperature in excess of ambient temperature, the process comprising injecting into the formation a water-external, aqueous surfactant mixture containing non-spherical micelles and being non-Newtonian at the temperature of use and having the characteristic of exhibiting a viscosity increase upon a temperature increase; the viscosity of the surfactant mixture being sufficient at the formation temperature to effect efficient fracturing of the formation, the aqueous surfactant mixture comprising 2 to 70% by volume hydrocarbon, at least 1.5% by volume surfactant, and 25% to 95% by volume of an aqueous medium, and injecting the surfactant mixture into the formation and effecting fracturing of the formation.

The water-external surfactant mixtures useful with this invention can be micellar solutions or microemulsions or "stable emulsions." By "stable emulsion" is meant a mixture that is phase stable for a relatively indefinite period of time, e.g. for at least two weeks. These particular mixtures are also non-Newtonian fluids, i.e. there does not exist a linear relationship between the shear rate and the shear stress, e.g. the apparent viscosity of the liquid decreases with increasing shear stress. Thus, the high shear rate in the pipe causes a low apparent viscosity and more fluid flows at a given pressure drop

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than would occur with a corresponding Newtonian fluid. As the fluid enters the formation, the shear rate decreases and the viscosity increases. This condition causes more effective fracturing. Besides the pseudoplasticity of these mixtures, the drag reduction characteristic of these surfactant mixtures permits high flow rates at minimum pressure drops.

10 The surfactant mixtures contain (by volume) less than 2 to 70%, preferably 2 to 55% and more preferably 2 to 40% hydrocarbon; 25 to 59%, preferably 40 to 95%, and more preferably 55 to 95% aqueous medium, at least 1.5% and up to 20% surfactant; and optionally 0.01 to 20% or more, and preferably 0.1 to 5% by volume of cosurfactant, and/or 0.001 or less up to 5% or more and preferably 0.01 to 2.5% by weight of electrolyte (based on the aqueous medium). Preferably 0.001 to 5.0% and more preferably 0.01 to 3% by weight, based on the aqueous medium, of a water-soluble, high molecular weight polymer is incorporated into the surfactant mixture. Examples of useful polymers includes nonionic polymers such as Stein Hall Polymer 1212A (a guar derivative polymer marketed by Stein, Hall and Co., Inc., 605 3rd Avenue, N.Y., N.Y. 10016).

30 The hydrocarbon can be crude oil, a partially refined fraction of crude oil, e.g. kerosene, gas oil, naphtha, etc.; refined fractions of crude oil, e.g. propane, butane, hexane, etc.; or a synthesized hydrocarbon, including alkyl substituted aryl compounds and halogenated hydrocarbons. The aqueous medium can be soft water, brackish water or a brine water. The surfactant can be cationic, anionic, or nonionic but must have at least some water-solubility and oil-solubility characteristics; preferably, the surfactant is a monovalent cation-containing petroleum sulfonate having an average equivalent weight within the range of 350 to 525 and more preferably 400 to 470. The cosurfactant can be an amine, aldehyde, ester, ketone, ether, but is preferably a hydroxy-containing compound (e.g. aliphatic alcohols, glycols, and alcohols containing an ether grouping(s) or like functional group) containing 1 to 20 carbon atoms and preferably 3 to 16 carbon atoms. The surfactant, cosurfactant, and hydrocarbon can be mixtures of components within their respective generic groups. The electrolyte is a water-soluble electrolyte and is preferably an inorganic base, inorganic acid or an inorganic salt.

55 The components of the surfactant mixture can be admixed in any suitable manner, e.g. stirring or agitation, shaking, pumping, etc. The surfactant mixture can be designed not to phase separate upon storage under wide temperature variations and can be prepared at the well site or any convenient place.

65 Viscosity of the surfactant mixture can be

varied over a wide range permitted by components of the surfactant mixture. Concentrations as well as the properties of the components influence the viscosity of the surfactant mixture. For example, the viscosity of a given surfactant mixture at a given temperature and shear rate can be increased from 72 cp to 460 cp by increasing the concentration of Stein Hall Polymer 1212A from 1% to 2%. Designing high viscosity mixtures for high temperature reservoirs can be done by formulating the surfactant mixture with different molecular weight and types of surfactants, cosurfactants, hydrocarbon; varying the concentration(s) of water, hydrocarbon, cosurfactant, electrolyte; etc.

Of course, the viscosity of the surfactant mixture desired in the reservoir will be dependent upon the permeability of the reservoir, temperature of the reservoir and other characteristics of the reservoir. Generally speaking, a relatively viscous surfactant fracturing fluid is desired to obtain an efficient fracturing process.

Propping agents may be incorporated into the surfactant mixture. The viscosity of the surfactant mixture is desirably high enough to facilitate keeping in suspension the propping agents. Examples of useful propping agents include coarse sand grain, tempered glass beads, metallic pellets such as aluminum pellets, and similar like materials. Such propping agents are usually present in concentrations of 0.1--5 lbs. per gallons and preferably 0.5--3.0 lbs. per gallon of fracturing fluid. Sizes of the propping agents generally range from 6 to 400, preferably 10 to 100 or more and more preferably 10 to 20 mesh. Of course, the particular reservoir will dictate the desired size of propping agents.

Fluid loss agents in concentrations of .001 to 2 lb/gal and preferably .01 to 0.2 lb/gal are useful with the surfactant mixtures. Such agents include silica flour (200 mesh silica sand), Atomite M-3 (ground calcium carbonate having diameters less than 15 micron, manufactured and marketed by Thompson, Weinman & Co., Cartersville, Georgia), and like materials. Silica flour is preferred.

Injection rates of the surfactant mixture will depend on downhole pressure, permeability of the formation, depth of the formation, etc. Such injection rates should be sufficient to cause the formation pressure near the well bore to exceed the "overburden pressure". For most reservoirs, the injection rates should be sufficient to obtain a formation pressure near the well bore of 500 to 5,000 psi--this will be sufficient for most reservoirs.

Prefracturing agents may be injected before the surfactant mixture to obtain desired effects. Examples of such include acids,

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aqueous acids, and other agents which tend to clean the rock face or the formation to permit a more efficient fracturing process. Also, diverting agents may be intermittently injected while injecting the surfactant mixture to obtain a more uniform fracturing profile — such is preferred in heterogeneous formations. Examples of diverting agents include tar derivatives, scaler balls in a cased well, etc.

The following Example illustrate specific working embodiments of the invention. Unless otherwise specified, all percents are based on volume and the properties of the surfactant mixture are measured at ambient temperature.

#### Example

A water-external micellar solution is obtained by mixing 1.6% Pyronate 50 (sodium petroleum sulfonate, marketed by Sonneborn Chemical Co., New York, N.Y., 50% active sulfonate, average equivalent weight 360); 1.8% Petronate HL (sodium petroleum sulfonate, marketed by Sonneborn Chemical Co., 62% active sulfonate, average equivalent weight 455%; 3.3% kerosene and 93.3% aqueous medium containing 0.93% by weight (based on water) NaCl. To this micellar solution there is added 1% of Stein Hall Polymer 1212A. The resulting mixture has a viscosity of about 72 cp. at 170°F. The concentration of the polymer is increased to 1.6% polymer and a viscosity of 328 cp. is obtained; at a polymer concentration of 2%, the viscosity of the aqueous mixture mixture is 460 cp. at 170°F. To illustrate how the viscosity increases upon an increase in temperature, the micellar solution containing 1.6% polymer was heated, it has the following viscosity profile:

Temperature (°F)	Viscosity (cp — 100 rpm) Fann Viscometer
74	313
100	336
150	378
170	328

For general purpose fracturing, the fluid desirably has a viscosity of 200 to 500 cp. when measured on a Fann Viscometer at 100 rpm at 170°F. The fracturing fluid should preferably have a fluid loss of under 30 milliliters after 30 minutes of flow through a given filter paper at 1,000 psi pressure and at 170°F. Also, the pumpability characteristics of the fracturing fluid are desirably like that of a 5 cp. fluid. In addition, the drop rate of propping agents within the fracturing fluids should be less than 2 feet per minute for 10 mesh glass beads.

To determine the properties of these surfactant mixtures, the following tests were used:

Fluid loss characteristics are measured using the procedure defined in API RP-13B, second edition, April 1969, but with the resistivity cell defined in U.S. Patent 3,617,869 to Beitel et al and operated at 850 psig. A "Specially Hardened Filter Paper for Baroid Filter Processes", Catalog No. 988, 2 1/2 in. diameter, marketed by Baroid Division, National Lead Company, Houston, Texas, was used as the filter paper.

The drop rate of the surfactant mixture was determined by observing the time required for a 10 mesh glass bead to drop through the fluid contained in a 200 ml. graduated cylinder.

The pumpability of the fracturing fluid was determined from a mathematical relationship based on data obtained from a capillary tube or 30.33 centimeter length and 0.003365 centimeter in radius. These data were fed to a computer program from which the pumpability of the fluid was determined.

The properties of the fluid identified in the Example were determined: the best pumpability for this particular fluid was found to be 43.5 cp and the drop rate was less than 0.008 feet per minute. The fluid without a fluid loss agent exhibited a fluid loss of 150 ml/30 min; but, with 0.02 lb of silica flour/gal of micellar solution, the fluid loss was 20.5 ml/30 min for the standard API test. As mentioned earlier, this fluid contains a nonionic polymer.

#### WHAT WE CLAIM IS:—

1. A process of hydraulically fracturing a subterranean hydrocarbon bearing formation penetrated by at least one well, the formation being at a temperature in excess of ambient temperature, the process comprising injecting into the formation a water-external, aqueous surfactant mixture containing non-spherical micelles and being non-Newtonian at the temperature of use and having the characteristic of exhibiting a viscosity increase upon a temperature increase, the viscosity of the surfactant mixture being sufficient at the formation temperature to effect efficient fracturing of the formation, the aqueous surfactant mixture comprising of 2 to 70% by volume hydrocarbon, at least 1.5% by volume surfactant and 25% to 95% by volume of an aqueous medium, and injecting the surfactant mixture into the formation and effecting fracturing of the formation.

2. A process according to claim 1, wherein the surfactant is a petroleum sulfonate having an average equivalent weight within the range of 350 to 525.

3. A process according to claim 1 or 2, wherein the surfactant mixture contains a propping agent.

4. A process according to Claim 1, 2 or 3, wherein the surfactant mixture comprises a

cosurfactant, an electrolyte, or a cosurfactant and an electrolyte.

- 5 5. A process according to Claim 4, wherein the concentration of cosurfactant is 0.01 to 20% by volume and the concentration of electrolyte is 0.001 to 5% by weight (based on the aqueous medium).

- 10 6. A process according to any one of the preceding claims, wherein a diverting agent is intermittently injected into the formation during the injection of the surfactant mixture to effect a more uniform fracturing profile.

- 15 7. A process according to any one of the preceding claims, wherein the aqueous phase of the surfactant mixture contains 0.001 to 5% by weight, based on the aqueous medium, of a water-soluble high molecular weight polymer to impart a viscosity increase to the surfactant mixture.

- 20 8. A process according to claim 7, wherein the polymer is non-ionic.

9. A process according to any one of the preceding claims, wherein the aqueous surfactant mixture comprises 2% to 55% by

25 volum hydrocarbon, 40% to 95% by volume aqueous medium, 1.5 to 20% by volume of monovalent, cation-containing petroleum sulfonate having an average equivalent weight within the range of 350 to 525, and 0.001 to 5% by weight, based on the aqueous medium, of a water soluble high molecular weight polymer.

- 30 10. A process according to any one of the preceding claims, wherein the surfactant mixture comprises a fluid loss control agent.

- 35 11. A process according to claim 10, wherein the fluid loss control agent is silica flour in an amount of 0.001 to 2 pounds per gallon of surfactant mixture.

- 40 12. A process according to claim 1, substantially as hereinbefore described in the Example.

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Printed for Her Majesty's Stationary Office, by the Courier Press, Leamington Spa, 1975.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AS, from which copies may be obtained.